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THE AQUEOUS GEOCHEMISTRY OF ARSENIC

FINAL PROJECT REPORT TO THE U.S. BUREAU OF LAND MANAGEMENT AND BARRICK-GOLDSTRIKE

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INTRODUCTION

The purpose of this research project was to carry out laboratory investigations designed to elucidate the geochemistry of various forms of arsenic in aqueous solutions. The two main goals of the research are to: 1) determine the kinetics and mechanism of reduction of As(V) to As(III) by sulfide; and 2) measure the solubility of As(III)-sulfide phases and elucidate the thermodynamics and stoichiometry of thio-arsenite species in aqueous solutions via solubility and Raman spectroscopic methods. This information will aid in the prediction of the behavior of As in environments such as pit lakes and acid mine drainage. Moreover, the precipitation of As(III)-sulfides and/or the adsorption of As(III) onto mineral surfaces may represent viable mechanisms for the removal of this toxic element from hydrometallurgical waste streams and contaminated waters. This report summarizes the results we have obtained during this project (September 1, 1996-August 31, 1999

REDUCTION OF As(V) BY SULFIDE

BACKGROUND

Various pathways have been proposed for arsenate ($H_xAs^vO_4^{x-3}$) reduction, such as reduction and alkylation by *Methanobacterium* and *Desulfavibrio vulgaris* (McBride and Wolfe, 1971), and reduction by other anaerobic bacteria (Ahmann et al., 1994; Macy et al., 1996; Newman et al., 1997). Nonetheless, abiotic arsenate reduction processes should not be dismissed. Sulfide in the form of H_2S or HS^- is frequently present at appreciable concentrations in reducing environments and is a strong reductant (see for example Morse et al., 1987). Based on standard-state redox conditions, hydrogen sulfide (H_2S) should be capable of reducing arsenate ($H_2AsO_4^-$ or $HAsO_4^{2-}$) to arsenite (H_3AsO_4)—reaction 1.

$$H_2AsO_4^- + H_2S + H^+ \Leftrightarrow H_3AsO_3 + 1/8S_8 + H_2O \qquad (1)$$

Where, based on the free energies of formation provided by Wagman et al. (1982), $\Delta G^o_{rxn} = -100.5$ KJ/mol.

Newman et al. (1997) noted that the kinetics of arsenate reduction by sulfide at pH 6.8 are slow (second-order rate constant, k_{pH7}, of 1.04 M^{-1} d^{-1}). However, other pH values were not considered and the conversion of sulfide from HS^- to H_2S below pH 7

could vastly change the interactions of sulfide with arsenate. For instance, within 33 h nearly complete conversion of arsenate to arsenite occurs at pH 4 while less than 10% occurs at pH 7 with initial sulfide:arsenate molar ratios of roughly 10^4: 1 (Cherry et al., 1979). Furthermore, arsenate reduction to arsenite has been observed in fjord waters at a depth where H_2S is dominant over O_2 (Peterson and Carpenter, 1983).

Once reduced, As(III) may also form soluble and insoluble arsenic-sulfide complexes. Several soluble arsenic-sulfide complexes, such as arsenic monomers with two and three sulfur atoms (with and without oxygen), as well as dimeric and trimeric arsenic-sulfur complexes, have been described or suggested during orpiment (As_2S_3) dissolution (Mironova et al., 1980, 1984, 1990; Spycher and Reed, 1989, 1990a and b; Krupp, 1990a and b; Helz et al., 1995). Because of the environmental significance of arsenic redox reactions and the potential for reacting with sulfide in acidic systems, we conducted this study to determine the kinetics and reaction paths of arsenate with dissolved sulfide.

EXPERIMENTAL SECTION

Kinetic Experiments

We first explored the effect of sulfide and arsenate concentrations on the ensuing redox reaction. Sodium arsenate was added to 0.1 M acetate buffer to obtain a concentration of 133 μM arsenate. Buffered (pH 4, 5, or 7) arsenate solutions in glass bottles were placed in a nitrogen-purged glove box along with a concentrated solution of sodium sulfide; dissolved sulfide was added to the buffered arsenate solutions in the glove box to obtain inital sulfide concentrations of 13.3, 26.6, 133, and 266 μM sulfide, yielding sulfide:arsenate ratios of 1:10, 1:5, 1:1, 2:1, respectively. Solution pH and Eh were determined and then the bottles were capped and placed on a shaker at 150 rpm for *ca.* 96 h, after which the samples were filtered through 0.22-μm pore filters. These experiments were performed in duplicate at 24° ± 2° C.

To obtain greater detail on the reduction of arsenate by sulfide, we investigated the reaction at pH 4 and an initial sulfide:arsenate ratio of 2:1 (266:133 μM) while sampling more frequently and obtaining three replicates. Separate experiments, differing only with respect to the sample times and speciation methods, were performed for

arsenate and sulfide analysis. Subsamples of the buffered arsenate/sulfide solutions were filtered and analyzed at times from approximately 1 to 73 h; a simple forth-order polynomial ($r^2 > 0.99$) was used to extrapolate the sampling times and quantities of arsenate.

Two experiments were performed with higher S:As ratios. In one case the S:As ratio was 100:1 (S^{II-} 13.3 mM : As^{V} 133 μM) at pH 7 (TRIS/HCl); samples were withdrawn after 7 days. The other experiment was performed at pH 4 (0.1 M acetate buffer) and S:As 20:1 (S^{II-} 2660 μM : As 133 μM). Samples were withdrawn at 28.5 h and 32 h.

Chemical Speciation and Analysis

Arsenic speciation was performed with an ion chromatographic (IC) / hydride gas generation (HGG) / inductively-coupled plasma spectrometric (ICP) method, based on the IC / HGG / atomic absorption spectrometric (AAS) method of Manning and Martens (1997). Total solution arsenic was determined by conventional ICP spectrometry.

Dissolved sulfide (as H_2S, HS^-, and S^{2-}) was analyzed colorimetrically at 670 nm by the method of Golterman (1970). Samples were analyzed by ion chromatography with a Dionex DX500 ion chromatograph for sulfate, sulfite, thiosulfate, and polythionates, using a method described by Patterson et al. (1997).

Raman spectroscopy was used to identify reaction intermediates; spectra were recorded with a Kaiser Optics HOLOPROBE Raman spectrometer connected via a fiber-optic link to a solution cell. Samples were prepared for analysis using an S:As solution ratio of 2660 μM : 1330 μM to allow detection of arsenic-sulfur solution species.

Solid-Phase Analysis

The valence state and bonding environment of As in the precipitates was examined using XANES spectroscopy. Samples were prepared for XANES analysis by filtering the suspensions to deposit the solids on a 0.45 μm filter membrane, which was then affixed to a slotted Plexiglass holder (3.8 x 0.5 x 0.003 cm) and sealed with a mylar window. Samples were analyzed at the Stanford Synchrotron Radiation Laboratory (SSRL), Stanford, CA, on beam line (4-3).

RESULTS AND DISCUSSION

Reaction Rate and Initial Products

The reduction rate of arsenate by dissolved sulfide is highly pH-dependent, the rate being inversely related to pH (i.e., the reaction is more rapid under acidic conditions). Even at initial sulfide:arsenate ratios of 100:1, essentially no reduction was observed after 7-d at pH 7 (data not shown). Thus, to elaborate on the rate and reaction mechanism of arsenate removal, we investigated the kinetics at pH 4 and a molar S:As ratio of 2:1.

The removal of both arsenate and dissolved sulfide from solution at pH 4 is rapid, with almost complete removal of each within 20 h (Figure 1). The decrease in dissolved concentrations over the initial reaction period conformed to a second-order rate expression, being first-order with respect to both arsenate and dissolved sulfide (Figure 2),

$$d\,[H_2AsO_4^-] / dt = k\,[H_2AsO_4^-]\,[H_2S] \qquad (2)$$

which is consistent with reaction 1. The second-order rate constant, k_{pH4}, for the removal of arsenate is $3.2 \times 10^2\ M^{-1}\ h^{-1}$, which is 300X greater than that observed by Newman et al. (1997) at pH 7. However, neither the production of elemental S nor arsenite are noted with the disappearance of arsenate (Figure 3). The discrepancy between dissolved arsenate and arsenite compared with total dissolved arsenic (which decreases slightly as discussed below) concentrations imply that other aqueous arsenic species must be present. It appears that other dissolved As complex(es), possibly an As-S complex, are produced and that the mechanism of arsenate reduction by dissolved sulfide involves multiple steps.

On the basis of reaction stoichiometries and ion chromatograms, we propose the following initial reaction sequence of arsenate and hydrogen sulfide:

$$H_2AsO_4^- + H_2S \Leftrightarrow H_2AsO_3S^- + H_2O \qquad (3)$$

$$H_2AsO_3S^- + H_2S \Leftrightarrow H_2AsO_2S^- + 1/8S_8 + H_2O \qquad (4)$$

$$H_2AsO_2S^- + H_2S \Leftrightarrow H_2AsOS_2^- + H_2O \qquad (5)$$

The initial ligand-exchange reaction (reaction 3) is followed by the thio-arsenate complex undergoing electron transfer (reaction 4) with subsequent ligand-exchange of the thio-arsenite leading to an oxo-thio arsenic(III) ($H_2AsOS_2^-$) species (reaction 5).

To further aid in identifying possible intermediate As-S complexes, we used Raman spectroscopy with the spectral assignments of Helz et al. (1995). Raman spectra (not shown) of our samples at t = 50 h consist of a strong band at 456 cm^{-1}, ruling out monomeric As-S complexes observed to have bands between 325 and 412 cm^{-1}–and which are dominantly below 390 cm^{-1} (Helz et al., 1995). The higher shifts in our spectrum obtained at pH 4 are consistent with theoretically predicted bands for the trimeric As-S species $H_3As_3S_6$.

Our observations suggest the development (oligomerization) of a trimer upon reduction of arsenate by excess sulfide, leading us to include the following reaction (reaction 6) to the sequence.

$$3H_2AsOS_2^- + 3H^+ \Leftrightarrow H_3As_3S_6 + 3H_2O \qquad (6)$$

Combining the individual reactions presented above and the development of polysulfides, the overall reaction for the production of the trimeric thio-arsenic complex can be expressed:

$$3H_2AsO_4^-{}_{(aq)} + 12H_2S_{(aq)} \Leftrightarrow H_3As_3S_6{}^o{}_{(aq)} + 12H_2O + 3HS_2^-{}_{(aq)} \qquad (8)$$

This reaction does not, however, account for the production of arsenite that is observed to increase appreciably beyond 50 h and become the dominant aqueous As species beyond 140 h (Figure 2). Additionally, the S:As reactant ratio (4:1) in reaction 8 is unreasonable given the initial ratio of 2:1. To rectify both of these factors, we must propose a dissociation reaction of the trimeric arsenic-sulfur complex leading to the formation of dissolved arsenite (reaction 9).

$$H_3As_3S_6{}_{(aq)} + 9H_2O \Leftrightarrow 3H_3AsO_3{}^o{}_{(aq)} + 6H_2S_{(aq)} \qquad (9)$$

The overall expression representing the entire reaction sequence for soluble arsenic species may thus be expressed:

$$H_2AsO_4^-{}_{(aq)} + 2\,H_2S_{(aq)} \Leftrightarrow H_3AsO_3{}^o{}_{(aq)} + H_2O + HS_2^- \qquad (10)$$

which denotes the initial and final products and provides the correct As and S ratio of the reactants (1:2).

Finally, Very small quantities of orpiment are noted at this pH and As:S ratio (1:2); only when sulfide was in 10x or greater concentrations than arsenate did we note appreciable extensive precipitation of the orpiment phase.

Summary

In contrast to the slow reactions observed at neutral pH (noted here and in Newman et al., 1997), hydrogen sulfide is capable of reducing arsenate rapidly under mildly acidic conditions (pH 4)—being 300 more rapid at pH 4 than at pH 7. Therefore, an abiotic reduction pathway of arsenate may be appreciable in many surface environments. When such a reaction is operational, dissolved arsenic-sulfur complexes may account for sizeable levels of As, albeit as a transient phase, at moderate to low (<10:1) S:As ratios.

SOLUBILITY OF ARSENIC SULFIDE AND RAMAN SPECTROSCOPY OF THIOARSENITE SPECIES

BACKGROUND

The exact stoichiometry of thio-arsenite complexes remains controversial despite intense investigation. Spycher and Reed (1989; 1990a,b) proposed that the As(III)-sulfide species most consistent with the available literature at the time were the trimers $H_3As_3S_6^0$, $H_2As_3S_6^-$ and $HAs_3S_6^{2-}$. Krupp (1990a,b) emphasized some of the drawbacks of the approach of Spycher and Reed (1989) and favored, in analogy with Sb, some form of the dimer ($H_2As_2S_4$, $HAs_2S_4^-$, or $As_2S_4^{2-}$). Subsequently, new experimental solubility studies have been interpreted both in terms of the trimer $H_2As_3S_6^-$ (Webster, 1988; Eary, 1992) and the dimeric species (Mironova et al., 1990). Using EXAFS, Raman spectroscopy and *ab initio* molecular orbital calculations, Helz et al. (1995) have concluded that, in solutions undersaturated with respect to either orpiment or amorphous As_2S_3, monomeric species (i.e., $H_2AsS_3^-$ and $HAsS_3^{2-}$, actually formulated by Helz et al. as $AsS(SH)_2^-$ and $AsS_2(SH)^{2-}$) are predominant. However, Helz et al. (1995) reinterpret previous solubility experiments (Webster, 1990; Mironova et al., 1990; Eary, 1992) and suggest that at saturation the predominant species are the trimer $As_3S_4(SH)_2^-$ and the monomer $AsS(OH)(SH)^-$. Thus, the results of Helz et al. (1995) strongly support the possibility that the degree of polymerization of thio-arsenite species depends on the total As concentration in solution and that there may be a progression from monomers through dimers to trimers (to possibly higher polymers) as total As increases towards saturation with respect to an arsenic sulfide phase. Krupp (1988) has suggested the possibility of a similar progression for thio-antimony species.

It is apparent from this brief review of the literature that further work is required to completely resolve the nature and thermodynamics of thio-arsenite species. These properties of thio-arsenite species must be known in order to adequately predict the optimum conditions of removal of As(III) from contaminated waters and industrial waste streams by precipitation of solid As(III)-sulfide phases. In order to determine these properties, we conducted Raman spectroscopic and solubility studies.

EXPERIMENTAL METHODS

Solubility studies

Reaction apparatus: Experiments were conducted in three, one-liter glass reaction flasks, allowing three runs to be performed simultaneously. The primary concern with the reaction setup was that the experimental solution be completely isolated from atmospheric oxygen to avoid oxidation of either As(III) or sulfide. Temperature, pH, gas composition and pressure, and solution composition were monitored without opening the system to the atmosphere.

The composition of the gas phase in the reaction vessels was closely controlled. Individual reaction flasks were completely sealed from the atmosphere with glass heads using a Teflon gasket and stopcock grease. Gas was delivered to the reaction flasks by means of vinyl tubing connected to a plastic gas-control manifold. The manifold was connected directly to cylinders of H_2S and nitrogen gas. The nitrogen and H_2S could be delivered to the reaction flasks in any ratio. Nitrogen was used to purge the system of oxygen before and after opening. Gas constantly flowed through the system at a low rate to assure constant, known composition of the gas phase in the reaction flasks. Fresh gas entered the reaction vessels through a ground-glass joint fitting in the vessel head and bubbled through the experimental solution. Exhaust gas was collected from the vessel headspace above the solution through the same ground-glass joint fitting. The exhaust H_2S gas stream was then bubbled through gas wash bottles filled with dilute NaOH solution to trap as much of the H_2S as possible. Any gas remaining after treatment in the gas wash bottles was vented to the fume hood exhaust via vinyl tubing. The gas wash bottles provided backpressure that kept the pressure of the reaction vessels slightly above ambient.

The entire portion of each reaction flask that held the experimental solution was surrounded by a water jacket. Water from a Haake D-8 water bath was circulated through the jackets to control temperature. The exact temperature of the solution in the reaction flask was measured directly with a precision thermometer accurate to ±0.1°C. Each reaction flask was equipped with its own thermometer.

Solution pH was measured using an Orion Ross™ combination pH electrode model 81-02, selected for its tolerance to sulfide. The pH was measured directly in the reaction vessel without exposing the reaction solution to the atmosphere. This was accomplished using an airlock specifically constructed for the purpose that was installed in the top of the glass reaction vessel head.

The experimental solution could be sampled or altered without exposure to the atmosphere. A ground-glass joint stopcock was installed in the reaction vessel head. The stopcock was completely sealed when closed and was also fitted with a rubber septum during sampling. To sample the solution, the stopcock was opened and a length of clean capillary tubing was pushed through the septa at the top of the stopcock and fed down into the solution. The capillary tubing nearly filled the bore of the stopcock. The tight fit of the tubing, combined with the rubber septa and the positive pressure of the constant gas flow in the reaction vessels was sufficient to prevent atmospheric oxygen from contaminating the system during sampling. The sample was withdrawn using a Luer-Lock™ syringe connected to the capillary tubing.

pH measurement: Accurate pH measurement was achieved using pH buffers of the same ionic strength and at the same temperature as the experimental solution (I=0.1) to calibrate the pH electrode. This insured that the activity coefficient for H^+ is the same for the experimental solution and the buffer solutions. This procedure also minimized potential errors due to liquid junction effects. Three buffers were used to calibrate the electrode (CH_3COOH/CH_3COO^-; $H_3PO_4/H_2PO_4^-$; and $H_2PO_4^-/HPO_4^{2-}$). Buffer solutions were made from stock solutions of NaOH, H_3PO_4, CH_3COOH, and HCl that had been standardized by potentiometric titration. The titrant used to standardize the solutions was certified 0.1000±0.0005 N NaOH supplied by Fisher Scientific.

Sample collection and preservation: **O**nce equilibrium was reached within the reaction vessel, samples were collected without exposing the reaction vessel to the atmosphere by

using a 100 c.c. Luer-Lock ™ syringe and capillary tube. Samples were prefiltered using a 0.22 micron polypropylene filter fitted to the tip of the syringe. The 0.22 micron filters were thermally equilibrated and pre-hydrated by placing them in a sealed container filled with de-ionized water in the temperature control bath prior to sample collection. Some sample solution was used to flush the filter and syringe and then discarded before collecting the sample to be analyzed.

To retain quantitatively all the H_2S in the solution, the sample was injected from the syringe into and immediately sealed in a pre-weighed plastic bottle that contained pre-weighed aliquots of concentrated NaOH and H_2O_2 solution in excess of that needed to capture all H_2S by oxidation to sulfate (SO_4). The quantity of H_2O_2 solution was sufficient to oxidize all of the As^{3+} present and trap it as arsenate anion (AsO_4^{3-}, in which As is in a 5+ oxidation state). After a suitable equilibration time, excess H_2O_2 was then destroyed by heating at approximately 70°C for at least 4 hours. The sample was then analyzed for total arsenate and sulfate.

Analysis of samples for total As and S: Analysis for total As and total S was accomplished by anion chromatography. The preserved samples should have been fully oxidized. All As in solution should have been in the arsenate form (AsO_4^{3-}) and all S present in solution should have been in the sulfate form (SO_4^{2-}). Oxidized samples were analyzed for Cl^-, SO_4^{2-}, and AsO_4^{3-} using a Dionex™ DX-300 series ion chromatograph. Analysis was performed using an eluent composed of 180 mM sodium carbonate/170 mM sodium bicarbonate, run at constant concentration (isocratic conditions) through Dionex AG4A-SC and AS4A-SC guard and analytical columns

The chromatograph was calibrated at least once a day. Every tenth run was a quality control sample utilizing one of the calibration standards. Calibration standards used were approximately 0.1, 1.0, 10.0, 50.0, and 100.0 ppm (mg/Kg) concentration.

Raman spectroscopy

All solution preparation and manipulation was conducted in a low-oxygen, nitrogen-filled glove bag in order to minimize oxidation. Solutions were prepared in which the S/As ratio varied but the sum of the total arsenic and sulfide concentrations was held constant. A NaHS stock solution was prepared by bubbling H_2S gas through a solution of known NaOH concentration until measured pH was constant with time. A

sodium arsenite solution was prepared by dissolving reagent-grade $As_2O_3(s)$ in a NaOH solution. For a given set of experiments, the stock solutions of NaHS had the same sulfide concentration as the concentration of As in the stock sodium arsenite solutions. These two stock solutions were then mixed in various proportions to obtain solutions with S/As ratios of 9, 5.25, 4, 3.17, 1.94, 1.00, 0.515, 0.25 and 0.11. Two different sets of experiments were carried out: one in which $[As] + [S] = 0.1$ molal, and one in which $[As] + [S] = 0.5$ molal. In each set of experiments, the pH of each of the solutions was adjusted to a constant value using solutions of NaOH or HCl. A pH range from 13.2 down to approximately 7 was investigated. More acidic solutions could not be studied owing to precipitation of arsenic sulfide. Measurements of pH were conducted using an Orion Research Meter (Model SA250) with a Ross combination electrode, standardized against NIST pH buffers. An aliquot of each solution was placed in a glass NMR tube, and the tube was capped and sealed with parafilm. The Raman spectrum of each solution was acquired within 1-2 hours after being sealed in the NMR tube.

The Raman instrumentation has been described in detail by Marley et al. (1988) and Tait et al. (1991). Raman spectra were excited using the 514 nm line of a Spectra Physics Ar ion laser (model 2025-05) focused onto the sample with a cylindrical lens to match the monochromator slit. The laser delivered approximately 400 mW of power to the sample. The Raman scattering was viewed in a 135° backscattering configuration, with the scattered light collimated with a fast plano-convex lens (fl 1.3, planar side toward focussed spot on sample) and then subsequently focussed onto the slit of the monochromator (SPEX Triplemate, fl 6.3 input optics) with a second plano-convex f-matching lens (fl 6.5, planar side towards monochromator). The first two stages of the monochromator are locked in an additive-subtractive mode and function as a tunable bandpass filter, especially against the Rayleigh-scattered photons. The final stage disperses the inelastically scattered photons across a Princeton Applied Research model 1420 intensified silicon diode-array detector. The slit width of the monochromator was set at 140 μm. In general, 10 scans, each with a 10 s integration time, were co-added to improve the signal-to-noise ratio. Spectra were calibrated against standard peaks of toluene in methanol and the emission lines of a neon lamp. Spectral data were saved as

ascii files and subsequent data manipulations were carried out using PEAKFIT and SIGMAPLOT (Jandel Scientific).

RESULTS AND DISCUSSION

Solubility

Although a number of preliminary runs were conducted, no acceptable solubility data were collected during the course of this study. The reasons for this are: 1) It took the first two years to build the apparatus, and develop and test sampling, analytical and data reduction protocols; and 2) In the final year of the project, Pat Manion, the M.S. student responsible for this part of the project, suffered from severe emotional and physical illness which prevented him from completing the project. Although a technician was hired eventually to carry finish the experiments, it took him the remainder of the project period to learn the techniques involved, and in the end no data were collected. It is hoped that we can continue this part of the project as an unfunded research project in the year to come.

Raman spectroscopy

The All spectra exhibit a broad, asymmetric, relatively intense band from approximately 325 to 550 cm^{-1}(Fig. 4). Most of the intensity of this band can be attributed to Raman signals from the glass NMR tube, with a smaller contribution from librational motions of liquid water. Less intense bands centered near 625 and 800 cm^{-1} are observed in deionized water, and these are also attributable to water or the glass tube.

At $\Sigma S + \Sigma As = 0.1$ molal, pH = 13.2 and a S/As ratio of 9, a prominent, narrow band centered at approximately 383 cm^{-1} is evident, together with a low intensity shoulder on its high wavenumber side (Fig. 5). Upon a decrease in S/As ratio to 5.25, another narrow band, centered near 400 cm^{-1} emerges at the expense of the band at 383 cm^{-1}. At a S/As ratio of 4, the band at 383 cm^{-1} disappears. Between S/As = 4 and S/As = 0.25, the band at 400 cm^{-1} loses intensity, while a band centered near 420 cm^{-1} becomes relatively more prominent, until it too loses intensity. Meanwhile, broad bands near 600 and 800 cm^{-1} increase in intensity. At S/As = 0.11, the bands in the 350-450 cm^{-1} range disappear, leaving only the broad band observed in the background spectrum, and bands of increased intensity near 600 and 800 cm^{-1}. The broad bands observed at 600 and 800 cm^{-1} may be assigned to $HAsO_3^{2-}$ and AsO_3^{3-} according to the previous Raman

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measurements of Loehr and Plane (1968). The bands observed in the region 350-450 cm^{-1} can be attributed to As-S bonds (cf. Rogstad, 1972; Mikenda et al., 1982; Helz et al., 1995). These species may be pure thio-arsenites, or mixed species such as AsO_2S^{3-}, for example.

In solutions with $\Sigma S + \Sigma As = 0.1$ molal and pH = 12.6, only one prominent band is noted in the spectral region 350-450 cm^{-1}, but the maximum of this band appears to shift from about 383 cm^{-1} to 396 cm^{-1} as the S/As ratio varies from 9 to 0.25 (Fig. 6). The band is asymmetric to the high wavenumber side, and there may also be some intensity above background on the low wavenumber side. All of these observations suggest the presence of more than one component to the band. Similarly to pH = 13.2, as the S/As ratio decreases, bands near 600 and 800 cm^{-1} increase in relative intensity, suggesting the formation of arsenite species.

At $\Sigma S + \Sigma As = 0.1$ molal, pH = 10.5 and S/As = 9.0, there are two prominent bands in the low wavenumber region: one with a peak near 383 cm^{-1} and one near 412 cm^{-1} (Fig. 7). There is also a low intensity band near 325 cm^{-1}. As S/As ratio decreases, the intensity of the bands at 325 and 412 cm^{-1} increase at the expense of that at 383 cm^{-1}. With further decrease in S/As ratio, a very weak band appears near 420 cm^{-1} and then disappears, and we also observe a broad, intense band at about 790 cm^{-1}, which can be attributed to an arsenite species ($HAsO_3^{2-}$). For solutions with $\Sigma S + \Sigma As = 0.1$ molal and pH = 8.4-8.5 (Fig. 8), the low wavenumber portion of the spectrum behaves very much like that at pH = 10.5. However, in the region 600-700 cm^{-1} the spectrum closely resembles that attributed by Loehr & Plane (1968) to H_3AsO_3(aq).

If $\Sigma S + \Sigma As$ is increased to 0.5 at pH = 12.5-12.8 and S/As = 9.0, we observe a main asymmetric band in the low wavenumber region centered near 383 cm^{-1}, with a tail toward the low wavenumber side (Fig. 9). There is also a low intensity band centered near 310 cm^{-1}. With decreasing S/As ratio a shoulder appears on the 383 cm^{-1} band near 370 cm^{-1}. We have not observed previously any bands centered near 370 cm^{-1} at any pH or S/As ratio at $\Sigma S + \Sigma As = 0.1$ molal. Thus, we conclude that the species responsible for the shoulder at 370 cm^{-1} must be yet another thio-arsenite species containing a greater number of As atoms than any species previously detected. As S/As ratio decreases from 4.0 to 0.25, the relative intensities of the 383 cm^{-1} band and the 370 cm^{-1} shoulder do not

appear to change greatly, although the intensities of both decrease relative to bands attributable to arsenite species at 600 and 800 cm^{-1}.

Our Raman measurements provide evidence for the existence of at least five different S-bearing As species under the conditions of our experiments. We observe at least five independent Raman bands in the S-As stretching region of the Raman spectrum, centered near 370, 383, 400, 412 and 420 cm^{-1}. Additional species may exist but we cannot confirm their existence from our data. Also, other species may exist in more acidic solutions which were not studied here. Our results suggest that some of the confusion in the literature regarding speciation may be due to the existence of a series of thio-arsenites with differing degrees of polymerization. We also observe the conversion of thio-arsenites to arsenites as S/As ratio of the solution is lowered. Additional Raman and solubility measurements, required to establish the exact stoichiometries of the S-bearing As species, are in progress in our laboratory.

Helz et al. (1995) studied a solution containing 1 M NaHS and 0.08 M As at pH 8.2 and 12 at 25°C. They observed only three bands over the range 150-750 cm^{-1} at 325, 382 and 412 cm^{-1}. Upon an increase in pH from 8.2 to 12, the relative intensity of the band at 382 cm^{-1} increased at the expense of the two bands at 325 and 412 cm^{-1}. Based on ab initio calculations, Helz et al. (1995) attributed the bands at 382 cm^{-1} to the species $AsS_2(HS)^{2-}$ and the bands at 325 and 412 cm^{-1} to the species $AsS(HS)_2^-$, which can be related to one another through a simple protonation reaction. Like Helz et al. (1995), we observe two main bands in the pH range 8.5-10.5, at about 383 and 412 cm^{-1}, and we also observe a relative increase in the intensity of the former band with increasing pH. However, we further observe that, at constant pH, the intensity of the band at 383 cm^{-1} decreases relative to that at 412 cm^{-1} with decreasing S/As ratio. This observation indicates the existence of two species with different S/As ratios, not just differing degrees of protonation. Thus, either two species exist under these conditions which differ both in S/As ratio and degree of protonation or several different species exist, at least some of which exhibit closely overlapping Raman bands.

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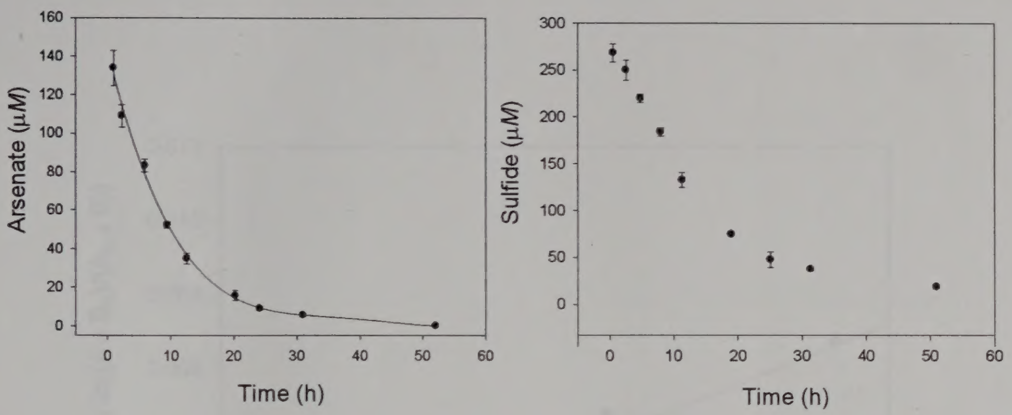

Figure 1. Dissolved arsenate and sulfide concentration as a function of time in pH 4 acetate buffer (initial arsenate=133 μM and sulfide=266 μM; predicted line, $r^2 > 0.996$, is a fourth-order polynomial used to equate arsenate to sulfide sampling times).

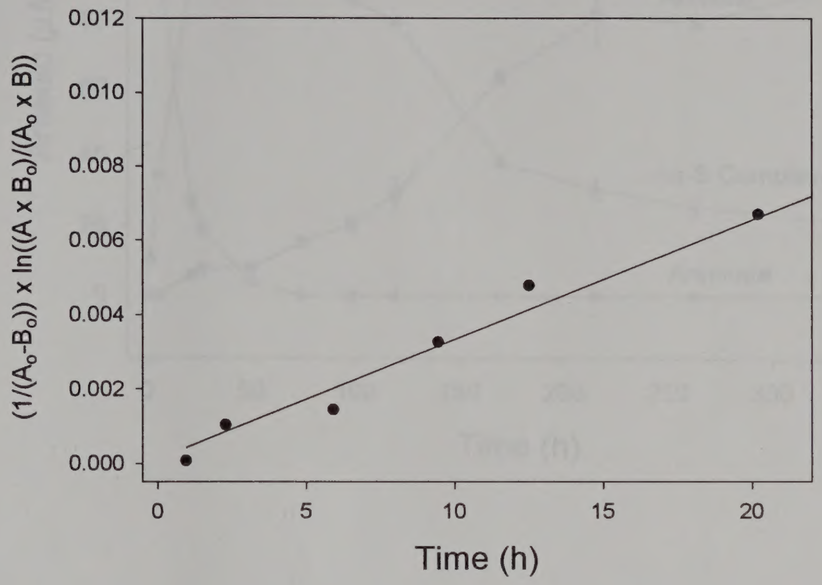

Figure 2. Second-order reaction (Eqn. 2) expression for the reduction of arsenate by dissolved sulfide with the predicted linear trend (on the abscissa, "A" denoted dissolved arsenate and "B" sulfide, with subscript "o" representing initial concentrations.)

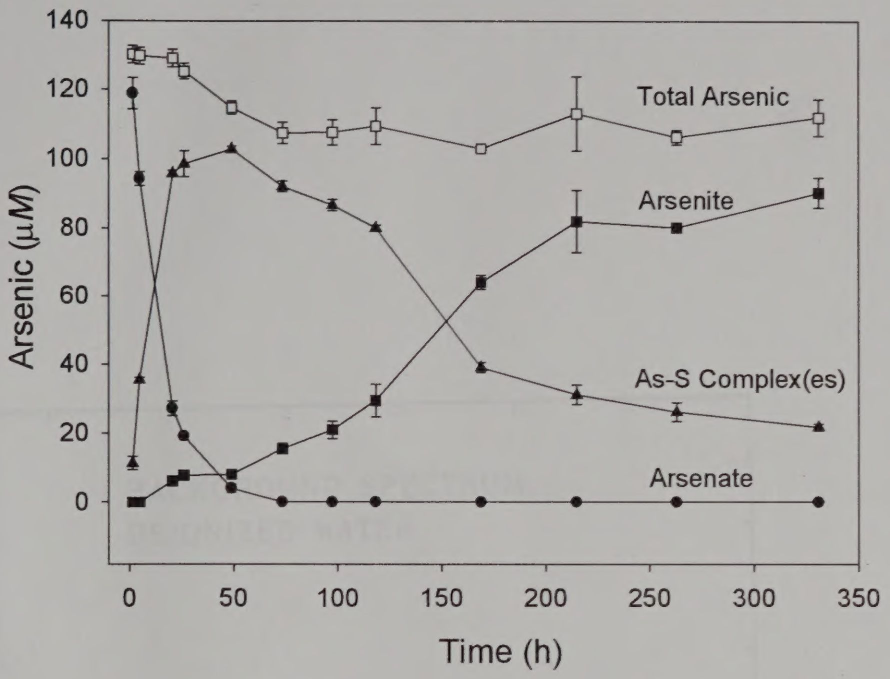

Figure 3. Dissolved arsenic species and total dissolved arsenic as a function of reaction time at pH 4. The initial arsenate and sulfide concentrations were 133 and 266 μM, respectively. The concentration of As-S complex(es) was (were) calculated by subtracting arsenate and arsenite concentrations from the total dissolved As concentration.

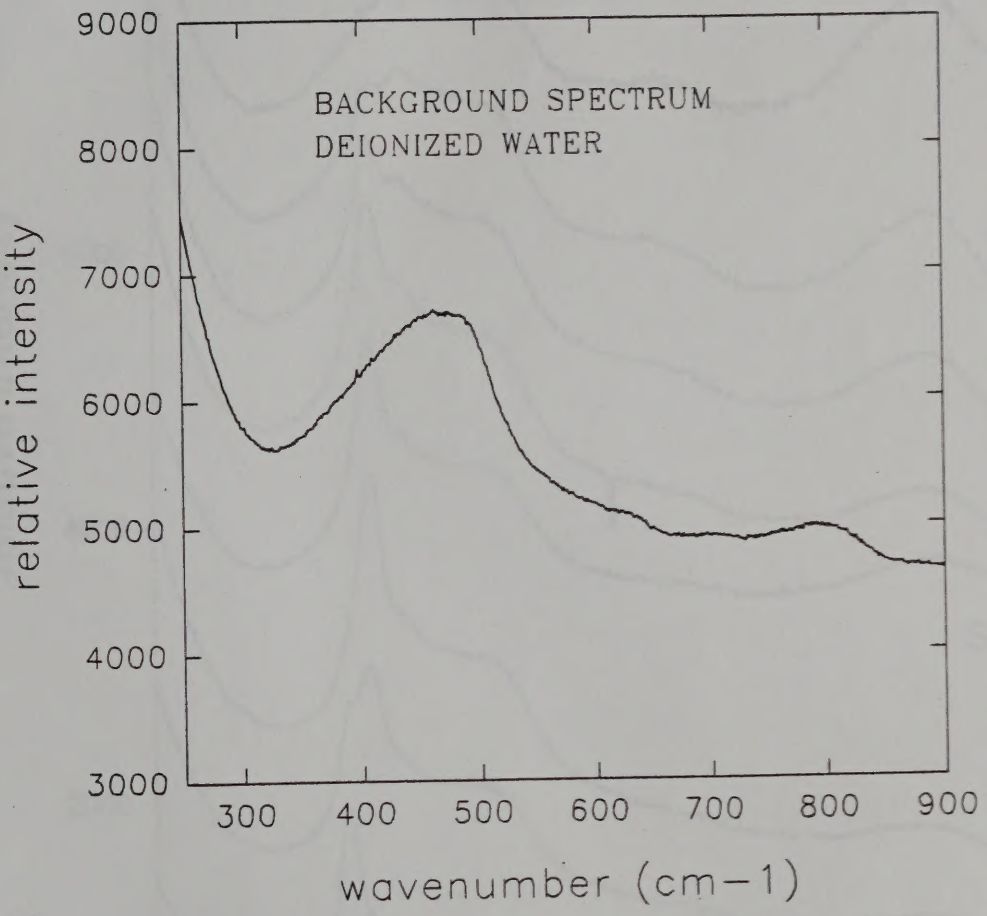

Figure 4 Raman spectra of deionized water taken in NMR tubes employed in this study.

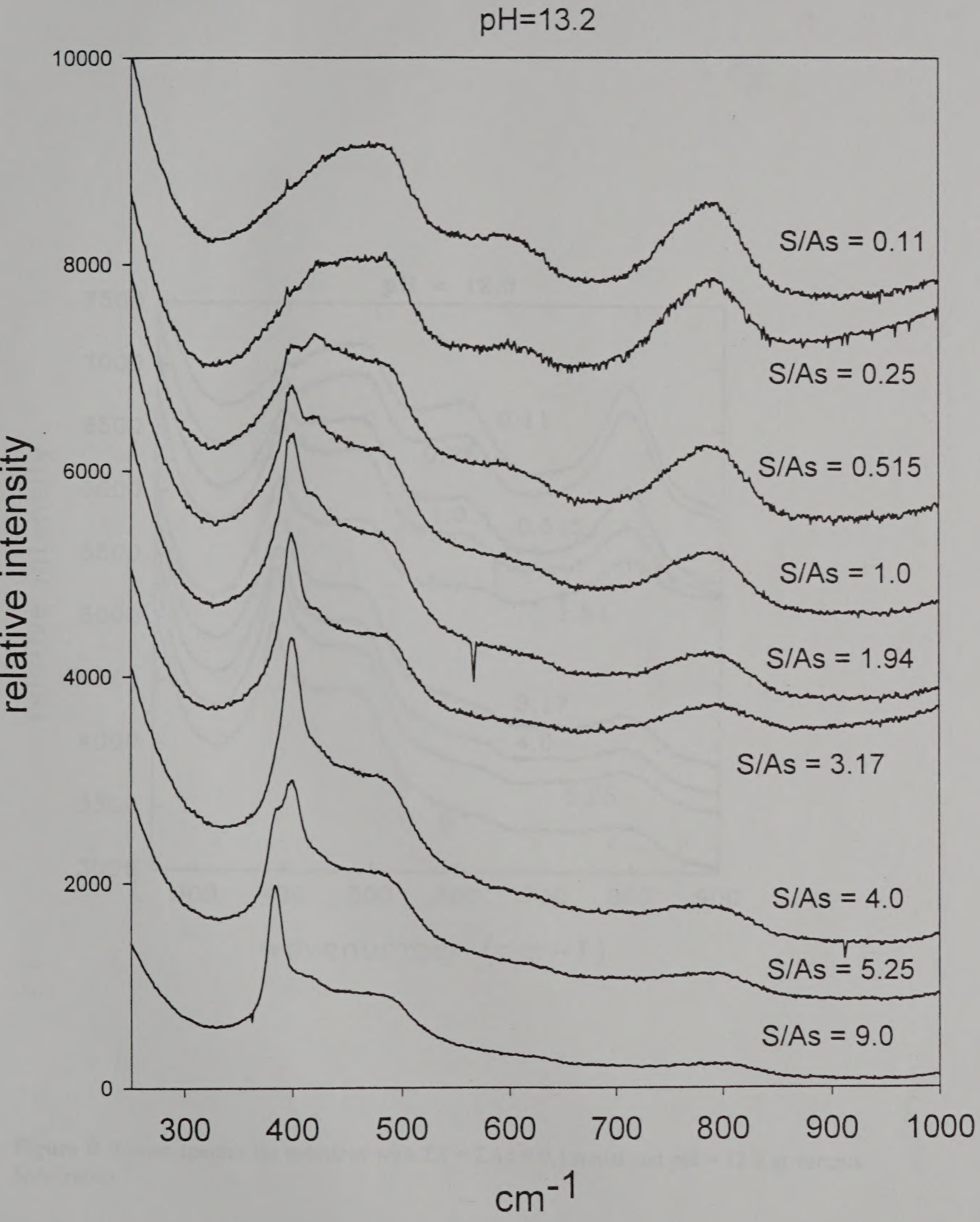

Figure 5 Raman spectra for solutions with $\Sigma S + \Sigma As = 0.1$ molal and pH = 13.2 at various S/As ratios.

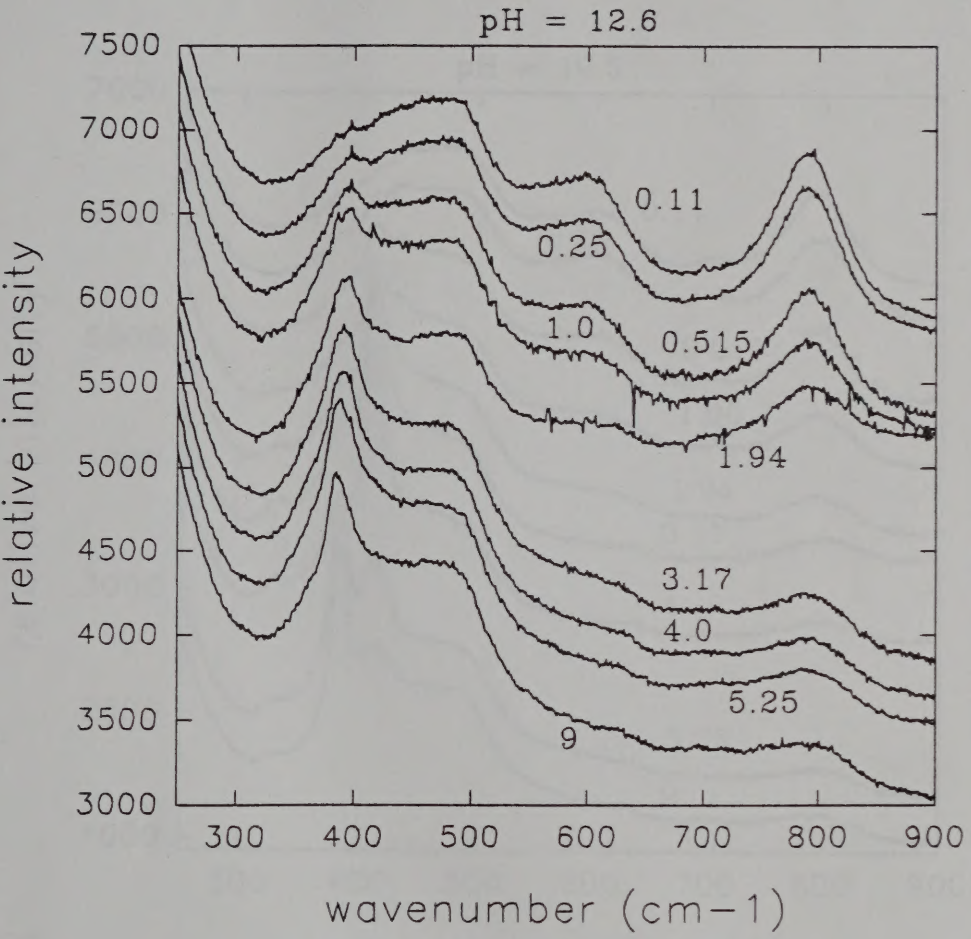

Figure 6 Raman spectra for solutions with $\Sigma S + \Sigma As = 0.1$ molal and pH = 12.6 at various S/As ratios.

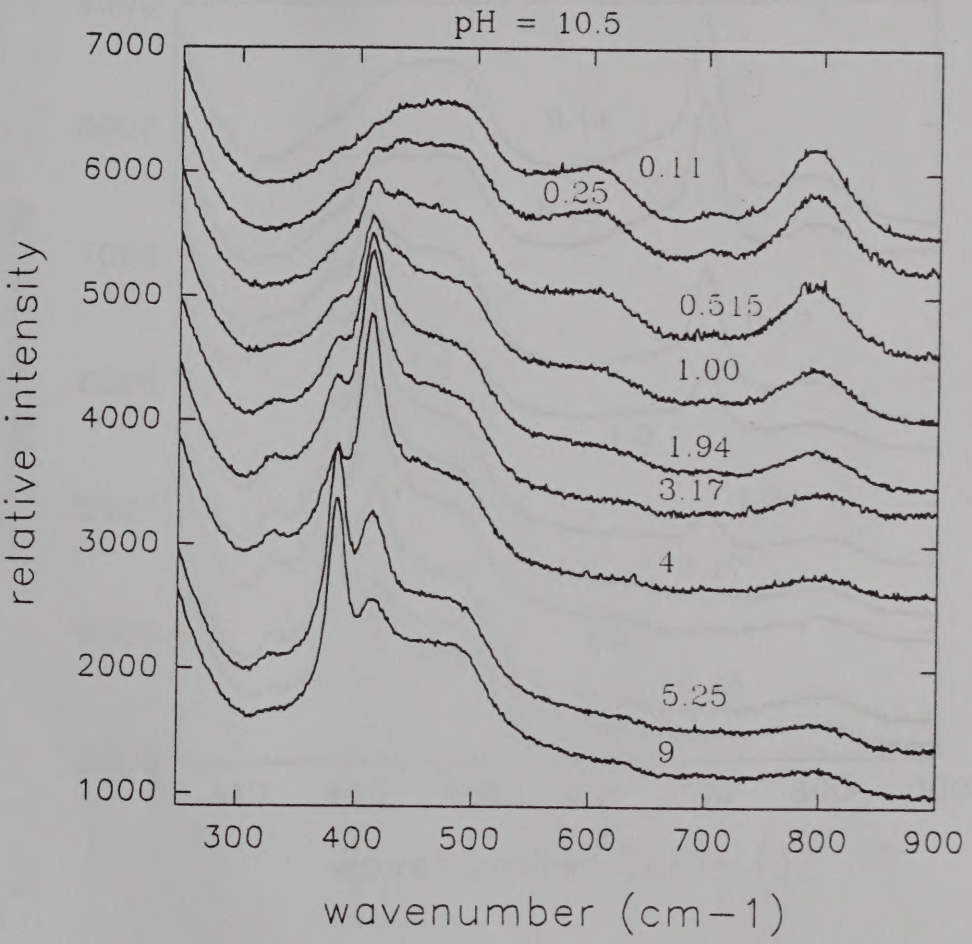

Figure 7 Raman spectra for solutions with $\Sigma S + \Sigma As = 0.1$ molal and pH = 10.5 at various S/As ratios.

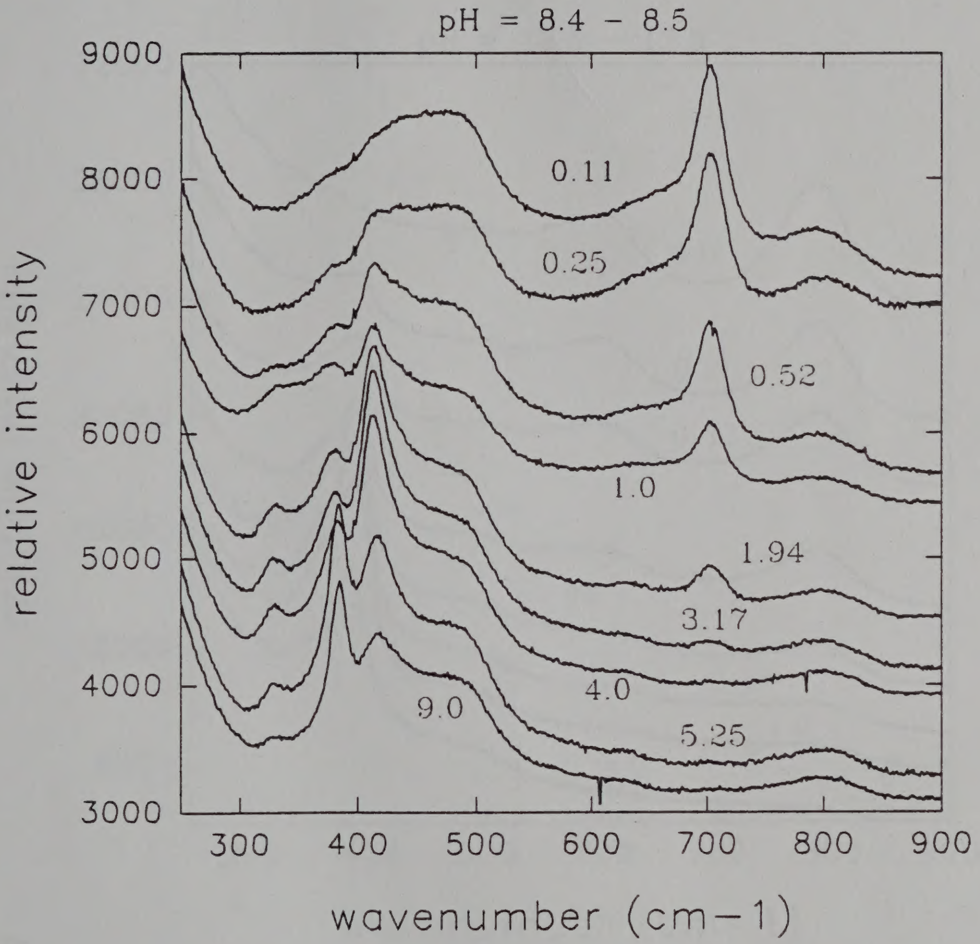

Figure 8 Raman spectra for solutions with $\Sigma S + \Sigma As = 0.1$ molal and pH = 8.4-8.5 at various S/As ratios.

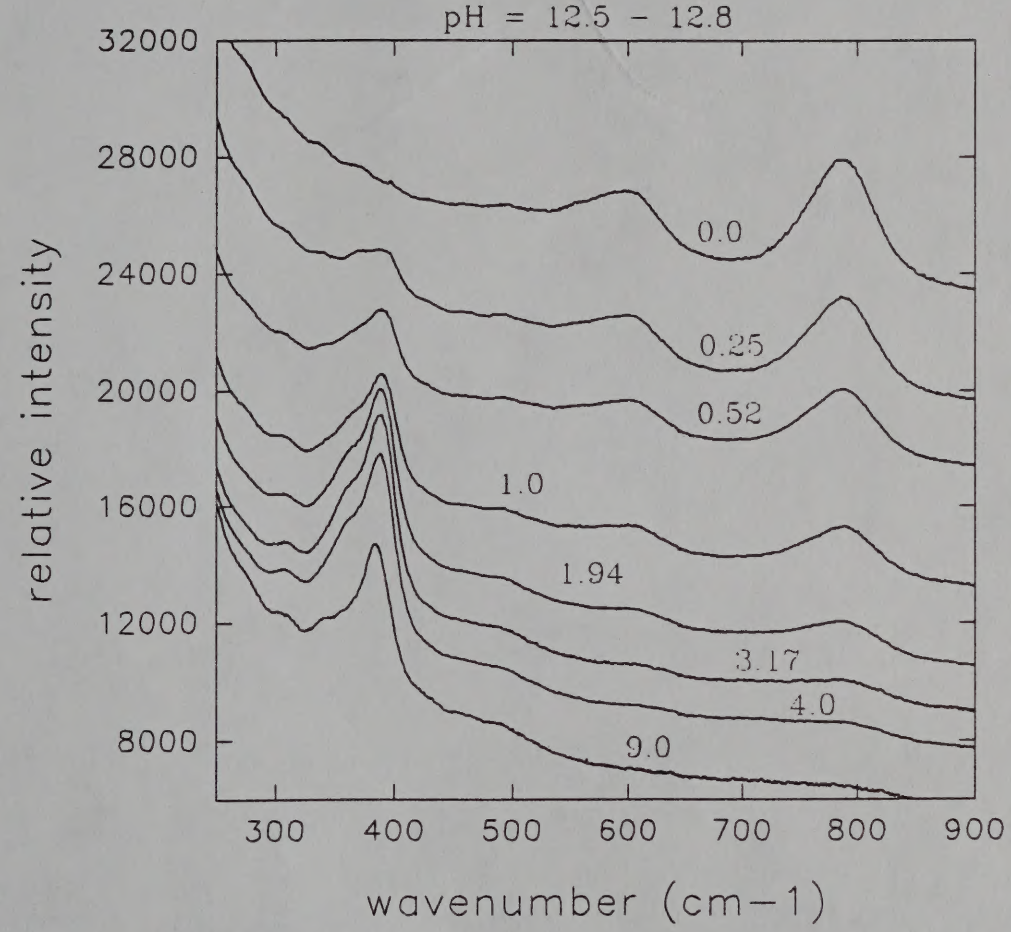

Figure 9. Raman spectra for solutions with $\Sigma S + \Sigma As = 0.5$ molal and pH = 12.5-12.8 at various S/As ratios.

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